

# Non-additive behavior of van der Waals dispersion forces due to material and surface geometry effects

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**Abstract.** We present a series of calculations of van der Waals (vdW) forces that show non-additive behavior. The results reveal effects of geometrical dependences of the dispersion forces, that are in strong contradictions to the results from additivity approaches like the Lennard-Jones (LJ) pairwise interaction and the proximity force approximation (PFA). For the simple geometries treated here deviations appear when the effects of the materials are taken into account. We obtain these results with a general and simple numerical method that allows for a detailed study of the vdW interactions. The method is also accurate and fast, and due to its generality makes the study of interactions between three-dimensional (3D) objects, with arbitrary geometries and configurations, feasible. We present results for normal, lateral and rotational forces.

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In recent years a perfection of chemical and physical methods has allowed for building so called nano-systems, in which the distances and sizes of the objects are of the order of tens of nanometers. One of the most interesting phenomena that emerge at this scale are the Casimir and vdW forces known as dispersion forces. They arise as a consequence of the quantum fluctuations of the electromagnetic fields. These forces have been measured experimentally at different conditions, and different theoretical methods have been developed for their study. The basic understanding of these interactions has increased in recent years but much of the physics of these phenomena need to be better known. The experimental success in measuring the Casimir forces [1] has opened up for an animated discussion and research about the possibility to develop nano-mechanical devices [2]. Now that subject has survived the speculative phase and several simple mechanical devices have been developed [3]. In order to understand, predict and design these devices it is necessary to study the dispersion forces between objects with different geometrical shapes, of different materials, and in different configurations. In doing so it is common to use more simple and accessible approximate methods that rely on additivity approximations. They are based on an assumption of a sort of additive interaction; the force is calculated as the sum of contributions from different parts of the system. As a consequence, one can only expect an increase in the interaction of the system when the dimensions of the objects are increased.

Here we develop a series of calculations of vdW forces for simple 3D objects. We treat cylinders, with circular and square cross sections, in different arrangements, interacting with each other or with a substrate; we study normal, lateral and rotational

forces. We show that when the effects of surface geometry and material are taken into account even these simple geometries show a non-monotonic and non-additive behavior. We have performed these calculations with the use of a new numerical method that is fast, easy to implement, and provides results with high precision. Its generality make it possible to apply on 3D finite objects with arbitrary form and orientation.

One of the more common methods based on additivity approximations has been formulated since the beginning of the study of the vdW interactions. It consists in the summation of the contributions from pairwise LJ interactions between the atoms of the different objects. This approach has, for example, recently been used to calculate the vdW forces between fullerenes and nanotubes [4]. For fullerenes the results have been compared with more realistic calculations and deviations of around 10% have been found [5]. Another additivity approach is the PFA. One discretizes the surface of the interacting objects in small parallel plane surfaces and treats the interaction between them like that of two infinite slabs. A sum of the forces between interacting pair planes gives the force between the objects. Rigorous theoretical models have confirmed the predictions of this model in the vdW case for dielectric spheres and cylinders [6]. In experiments agreements within 1% have been claimed [7]. More recent theoretical models have tried to determine the applicability of the PFA [8, 9] and external criterions for the formulation of the PFA have been postulated to extend its applicability [10, 9].

From the initial formulation of the Casimir force [11] one has come to realize the strong influence the geometry has on the properties of the system. Casimir showed that an interaction energy between two flat infinite plates arises from the variation of the zero point energy relative its value at infinite separation [11],

$$\mathcal{E}(z) = \frac{\hbar}{2} \sum_s \omega_s(z) - \frac{\hbar}{2} \sum_s \omega_s(z \rightarrow \infty),$$

where  $\hbar$  is Planck's constant and  $z$  the distance between the plates. In the general problem there is a dependence on the surface geometry and materials of the system due to the boundary conditions that the electromagnetic fields need to satisfy. In the idealized Casimir system only vacuum modes exist. For real metal objects both vacuum modes and surface modes contribute. The vacuum modes dominate the force in the retarded limit, the Casimir limit, and the surface modes in the non-retarded limit, the vdW limit.

Several theoretical methods have dealt with the problem of calculating the dispersion forces from the electromagnetic resonances of the system. The major part of them have been formulated for ideal perfect metals [12]. They have given an important insight into the physics of the phenomenon. However their results are not directly applicable to real systems. It has been shown that effects of the actual materials are important. In particular the surface plasmons are essential in the description of the phenomenon in the situation of close proximity of the objects [13]. The perfect metal model has no vdW range, which means that the results from this model only apply to experiments on actual micro-devices if the objects are far apart. Only recently a multipolar scattering formalism has been formulated for calculation of the interaction between dielectric objects [14]. These kind of methods give results with great accuracy over a wide range of distances for highly symmetric objects like spheroids or cylinders [15, 10, 16]. More complex geometries give rise to a more complex description with a slower computation convergency and low accuracy. A general numerical method for the

calculations of electric fields for arbitrary geometries and material has been developed [17]. However a deeper knowledge in advanced numerical methods is required in order to obtain results with reasonable accuracy and computational time: this hampers its general use.

A more simple but also more accurate theoretical method is required to go beyond the more basic geometries and configurations that characterize the recent results; it should also be able to deal with the effects of different materials. Here we are interested in and focus on systems with distances and sizes of tens of nanometers. From the practical point of view, given the great number of nano-systems, existing and in progress, this focus does not constitute a severe limitation on the use of the model. However, much of the qualitative behavior found here is expected to be found also in slightly bigger systems where the retardation effects only start to be important.

In what follows we present a general theoretical method based on the solution of a surface integral equation. This method has been used in the past to solve problems of scattering. We have here adapted it to the calculation of vdW forces. The geometries of the objects we study here are simple but thanks to this method it has been possible to develop novel calculations of lateral and rotational forces, from which very few results exist in the literature.

## 1. Formalism

Consider a finite object, immersed in the vacuum, of arbitrary form defined by the surface  $\Sigma$  and made of a non magnetic material with dielectric function  $\varepsilon(\omega)$ . In the non-retarded limit the behavior of the electromagnetic fields is determined solely by the electric potential. The solution of the 3D Laplace equation on the boundary of the object satisfies the Fredholm integral equation [18]

$$\phi^0(\mathbf{r}) = \frac{\varepsilon(\omega) + 1}{2} \phi(\mathbf{r}) + \frac{\varepsilon(\omega) - 1}{4\pi} \int_{\Sigma} d\mathbf{S} \mathbf{n}' \cdot \nabla G(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}'),$$

where  $G = 1/|\mathbf{r} - \mathbf{r}'|$  is the Green's function of free space,  $\mathbf{r}$  and  $\mathbf{r}'$  points on the surface,  $\Sigma$ , of the object, and  $\phi^0$  is the electric potential derived from exterior sources.

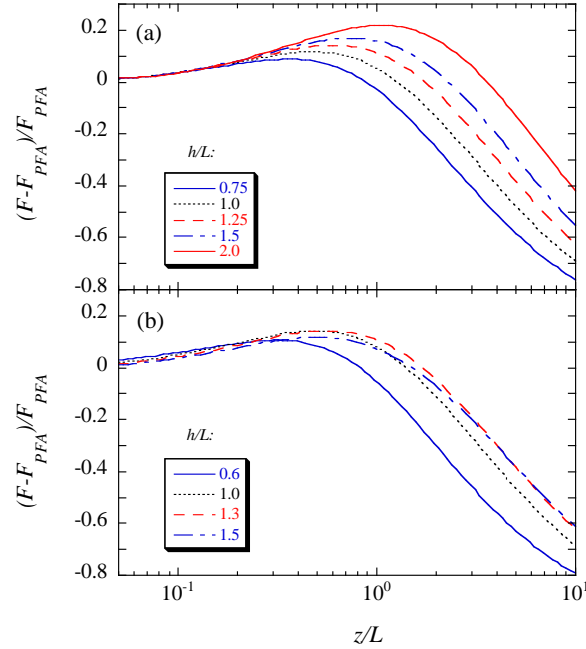
The properties of the kernel of this integral equation have been studied in the old potential theory [19]. Due to its properties it is possible to apply the theory of the Fredholm integral equation and the different analytical and numerical methods to its solution. Here we deal with the most simple numerical method, known as boundary element method. We have adapted it to obtain the resonances of the system, i.e., to find solutions different from zero when the applied external field,  $\phi^0$ , is identically zero. The method consists in the discretization of the surface  $\Sigma$  in  $N$  small planes of sizes  $\Delta s_i$  in the positions  $\mathbf{r}_i$  with normal unit vector  $\mathbf{n}_i$  and potential  $\phi_i$ . A homogeneous system of linear equations is obtained:  $\sum_j R_{i,j}(\omega) \phi_j = 0$ , with

$$R_{i,j}(\omega) = 2\pi \frac{\varepsilon(\omega) + 1}{\varepsilon(\omega) - 1} \delta_{i,j} + (1 - \delta_{i,j}) \frac{\mathbf{n}_j \cdot (\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} \Delta s_j.$$

The zero point energy of the system is given by

$$U(\omega) = -\frac{\hbar}{i4\pi} \int_{-i\infty}^{i\infty} d\omega \log \det R_{i,j}(\omega).$$

Note that there is no restriction on the shape and connectivity of  $\Sigma$ . Therefore, we can consider a surface that consists of two arbitrary non overlapping surfaces  $\Sigma_1$  and



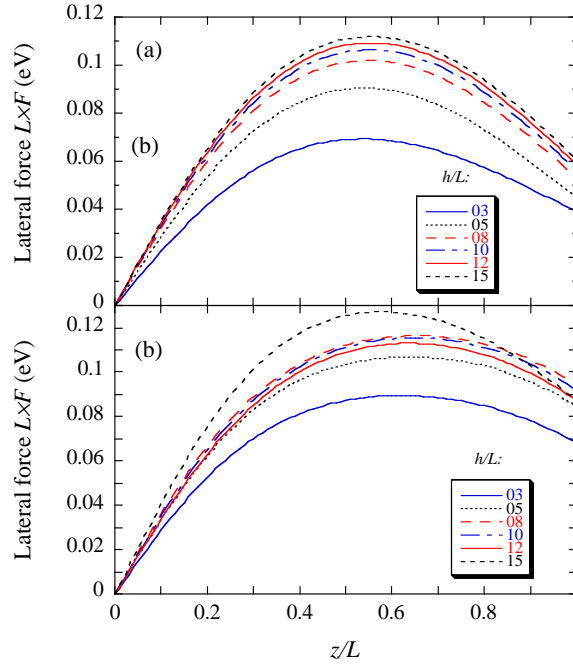
**Figure 1.** Normal forces between a finite gold cylinder and a gold substrate; (a) circular cross section with diameter  $L$ ; (b) square cross section with side length  $L$ .

$\Sigma_2$  with arbitrary positions and orientations. It is possible to study an object above a substrate by letting one of the objects be the mirror image of the other. The total energy of the system is obtained by numerically calculating the integral of the complete system and subtracting the value obtained considering the objects independently. The computational time goes like  $\mathcal{O}(N^2)$ , but  $N$  grows slower than in methods like that in [17], since our method is based on a discretization of a surface. With this method it is possible to, within a few hours, obtain results for the interaction energy with a precision of 1% at distances down to 5% of the diameter of the smallest of the objects. This conclusion we draw from comparisons with high precision calculations based on methods in [15].

## 2. Calculations and Results

In figure (1) we show results from calculations of the interaction between a gold cylinder and a gold substrate. The base of the cylinder is kept parallel to the substrate and at the distance  $z$ . Panel (a) is for cylinders with circular cross section of diameter  $L$  and panel (b) for square cross sections with side length  $L$ . The curves are for different heights,  $h$ . We have plotted the relative difference between our results and those from PFA. The PFA result is the force per unit area between two half spaces times the base area; it does not depend on the height at all.

First we observe in both panels that all the curves tend to zero in the small separation limit which means that all of them present the behavior of two parallel plates in the limit. At large distances a volume dependence is observed corresponding to dipolar interactions. This means that a larger cylinder has a stronger interaction

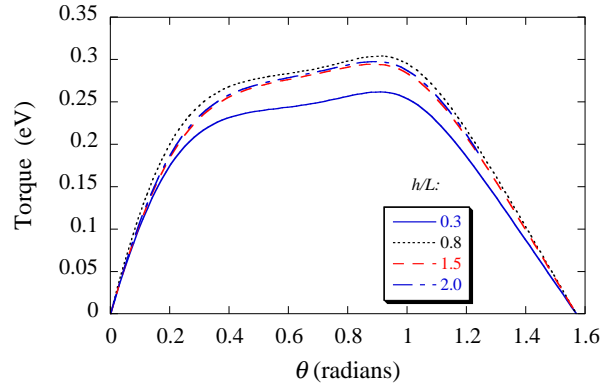


**Figure 2.** Lateral forces between two gold cylinders kept at the vertical separation  $L/2$  and moved horizontally the distance  $z$ ; (a) circular cross section with diameter  $L$ ; (b) square cross section with side length  $L$ .

with the substrate. At intermediate distances we observe that in the circular cylinder case, panel (a), the bigger cylinders always show a stronger vdW force. One can expect this behavior in an interaction that depends on the quantity of material, as is the case, for example, of an additive pairwise interaction. However the square cylinders in panel (b) show a completely different behavior: a non-monotonic relationship between the forces and the volumes of the objects. There are regions where an increase of the volume leads to a decrease in the force. For example at a distance smaller than  $0.8L$  the square cylinder with height  $1.5L$  is expected to show a greater force than the cylinder with  $h = L$ , but it does not. This indicates a sort of resonant behavior that depends on the geometry. These results agree with the geometry dependence of the resonant modes of the electromagnetic field.

This lack of direct relation between the force and volume of the object is also observed in the case of lateral forces. In figure (2) we show results from calculations of lateral forces between pairs of finite cylinders. Initially the cylinders are considered aligned above each other with parallel bases at a distance  $d = L/2$  from each other. Then there is a horizontal, lateral displacement  $z$  parallel to one of its sides of length  $L$  (in the case of cylinders with square cross section). The energy is calculated at different positions  $z$  and the lateral force is obtained through numerical derivation.

We observe that in the case of circular cylinders, panel (a) the objects with greater height show a greater lateral force than the objects with smaller height. Again this is the kind of behavior that one can expect through an additive interaction. However this is not always the case when one considers finite square cylinders. In panel (b) we present results for pairs of square cylinders of the same height. The



**Figure 3.** Torque between two gold cylinders with rectangular cross section,  $L \times 2L$ , and height  $h$ , kept at the vertical separation  $L/2$ .

lateral force increases in general with the height but for the cylinder of height  $1.5L$  the force is smaller than for cylinders of heights  $1.0L$ , and  $1.2L$  in a region of lateral displacements. Note, the wide region of linear behavior in the lateral force, which implies a harmonic oscillation around the completely aligned equilibrium. The PFA predicts a constant lateral force; it has been shown that this happens in the perfect metal case for periodic 2D steps for small normal separation [8]. However the non-constant linear form dominates the behavior of the dispersion forces when the objects are in close to alignment with each other even if they are in close proximity. This is a geometric dependence of the interactions between the borders of the objects that the PFA is not able to take into account.

In figure (3) we present results for rotational forces, or torques, between rectangular finite cylinders. The base is a rectangle with the longer side twice the length of the shorter. Each curve corresponds to a different height. Initially the cylinders are considered in their position of minimum energy where they are with their bases parallel and completely aligned. They are rotated around a perpendicular axis through the center of the bases. We calculated the energy at different angles and found the rotational force by numerical differentiation. We observe that the rotational force is not stronger for the greatest cylinder. The cylinder with height  $0.8L$  is of a sort of resonant height that gives the maximum rotational force. Also here, like in the lateral force, it is easy to see that the PFA will predict a constant rotational force in the proximity of the close alignment. However, one expects the non-constant linear behavior of the force close to the equilibrium position, independently of the proximity of the objects.

A non-monotonic behavior of the Casimir forces was also found in a recent work on perfect metal systems [17]. It involves complex interactions between walls and objects. Here we have shown that non-monotonic and non-additive behaviors can be seen in more simple systems when the effects of the materials are taken into account. These results are in conflict with those expected in PFA and from pairwise LJ interactions. Here, we have furthermore presented a method that constitutes a useful and versatile tool for the calculations of vdW forces in different configurations; it is able to deal with objects of different geometries and in different configurations; it gives fast and high precision calculations. The precision can be improved with an optimal discretization of

the surface and by exploiting the symmetries of the systems, like axial and translational symmetries. The method can be generalized to deal with systems that involve different materials.

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